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New processable polyaromatic amides were prepared from the acid chloride of bis-m-carboxyphenyl acetylene (V), the acid chloride of 1,4-bis-m-carboxyphenyl-1,3-butadiene (VI), and several aromatic diamines. The polyamides that contained acetylene units were cured by Diels-Alder cycloaddition reaction with 1,4-diphenyl-1,3-butadiene, whereas the polyamides with 1,3-butadiene units were cured with N-phenyl maleimide. Cured polyamides showed an increase in T_g, thermal, and heat stabilities. The polyamides can be cast into films and produce good glass-fiber laminates.

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New Processable Polyaromatic Amides Curable by Diels-Alder Cycloaddition

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Synopsis

New processable polyaromatic amides were prepared from the acid chloride of bis-*m*-carboxyphenyl acetylene (V), the acid chloride of 1,4-bis-*m*-carboxyphenyl-1,3-butadiene (VI), and several aromatic diamines. The polyamides that contained acetylene units were cured by Diels-Alder cycloaddition reaction with 1,4-diphenyl-1,3-butadiene, whereas the polyamides with 1,3-butadiene units were cured with *N*-phenyl maleimide. Cured polyamides showed an increase in t_g , thermal, and heat stabilities. The polyamides can be cast into films and produce good glass-fiber laminates.

INTRODUCTION

Curing processes that liberate gaseous side products have the deleterious effect of producing voids that substantially weaken laminates. Hence thermally stable laminating resins are needed that are not only low melting and moderately soluble before curing but can also be cured without giving off volatiles.¹ Particularly promising in this respect are polymers that contain substituted acetylene, butadiene, or both units in the backbone of the polymer chain.

Polymers with cyclic structures like aromatic or heteroaromatic ring systems have good thermal stability and high heat resistance. The problems of processability of cyclic-structured polymers are due to their low solubility in solvents and high melting temperatures. Therefore, this study is aimed at preparing new processable polyaromatic amides with good solubility before curing and with improved thermal, heat, and chemical resistances after curing.

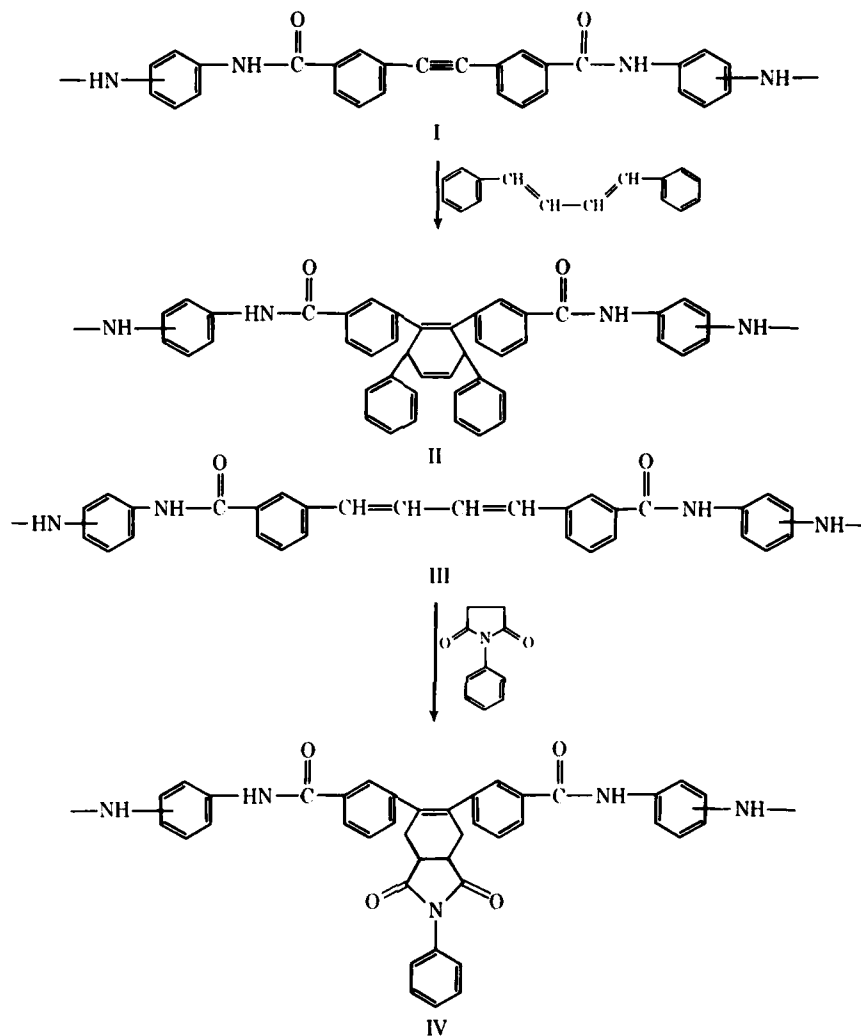
A hot drawing technique is commonly used in the fabrication process of aromatic polyamides, during which the physical structure of the polymers changes to produce high heat and chemical resistances in the resulting polyamides. The same purpose can be achieved by introducing a functional group on the chain backbone, which with the Diels-Alder cycloaddition reaction produces an improved heat and chemically stable polymer.

The acid chlorides of bis-*m*-carboxyphenyl acetylene (V) and 1,4-bis-*m*-carboxyphenyl-1,3-butadiene (VI) were synthesized for this study.^{2,3} These monomers were polymerized with different aromatic diamines in dimethylacetamide at 0°C. The polyamides that contained the acetylene moiety were cured by cycloaddition with 1,4-diphenyl-1,3-butadiene and those that contained

TABLE I
 Structure and Elementary Analysis of Polyamides

Polymer	Structure	Calcd				Found			
		%C	%H	%N	%S	%C	%H	%N	%S
P-I		78.10	4.14	8.28	—	74.48	4.17	8.08	—
P-II		78.10	4.14	8.28	—	73.36	4.40	8.20	—
P-III		70.29	3.76	5.85	6.69	67.48	3.83	6.00	6.84
P-IV		78.13	4.18	6.51	—	74.51	4.17	6.44	—
P-V		78.68	4.91	7.65	—	73.86	4.93	7.60	—
P-VI		78.68	4.91	7.65	—	69.70	4.91	7.82	—
P-VII		71.14	4.34	5.53	6.32	67.85	4.17	5.62	6.37
P-VIII		78.60	4.80	6.11	—	75.59	4.91	6.02	—

the butadiene moiety with *N*-phenyl maleimide as shown below.



The cured polyamides showed increased T_g , thermal, and heat stabilities.

EXPERIMENTAL

Acid Chloride of Bis-*m*-Carboxyphenyl Acetylene (V) and 1,4-Bis-*m*-Carboxyphenyl-1,3-Butadiene (VI)

Detailed procedures for the preparation of these monomers have been reported.^{2,3}

Aromatic Diamines

m-Diaminobenzene, *p*-diaminobenzene, and 4,4'-oxydianiline were purified by sublimation; bis(4-aminophenyl sulfone) was purified by recrystallization from ether.

General Procedure for the Preparation of Polyamides

Two millimoles of aromatic diamine was dissolved in 10 ml of dry *N,N*-dimethylacetamide (DMAC) in a 50-ml three-necked flask fitted with a stirrer, dropping funnel, and nitrogen inlet. The solution was cooled to 0°C and a stoichiometric quantity of diacid chloride in 5 ml of DMAC was added to the vigorously stirred solution of diamine under nitrogen. The solution became viscous. After 3 hr methanol was added and the precipitated polyamide was filtered and washed several times with methanol. The polymer was purified by dissolution in a small quantity of dimethylformamide, precipitated by adding methanol, filtered, washed, and dried at 100°C *in vacuo*. The yield was more than 90%. The polymers did not melt below 360°C.

Films and Glass-Fiber Laminates

Films and glass-fiber laminates can be made from solutions in dimethylformamide. The films were colored and brittle. The laminates look promising.

TABLE II

Polymer	$\eta^{30^\circ\text{C}}$ DMF + 5% LiCl	DSC thermogram (°C)	Softening temperature [(Vicat) °C]	Isothermal aging at 300°C for 3 days % wt loss
P-I	0.24 ^a	186	294	5.1
	— ^b	193	—	1.1
P-II	0.28 ^a	161	281	4.7
	— ^b	181	—	0.7
P-III	0.24 ^a	167	230	6.2
	— ^b	172	—	1.3
P-IV	0.18 ^a	157	217	7.1
	— ^b	161	—	1.2
P-V	0.20 ^a	173	301	2.9
	— ^b	184	—	0.3
P-VI	0.37 ^a	171	295	3.2
	— ^b	178	—	0.3
P-VII	0.29 ^a	169	265	4.3
	— ^b	172	—	0.8
P-VIII	0.21 ^a	160	262	4.1
	— ^b	165	—	0.9

^a Before curing.

^b After curing.

Curing

Polyamides that contained acetylene units were cured with 1,4-diphenyl-1,3-butadiene in refluxing dimethylacetamide under nitrogen for 24 hr. Polymers that contained the 1,3-butadiene group were cured with *N*-phenyl maleimide in refluxing dimethylacetamide under N_2 for 24 hr.

Oxidative Aging

Polyamides were heated in an air-circulated oven at 300°C for 3 days. The samples were weighed before and after aging and the percentage weight loss was determined.

Softening Temperature

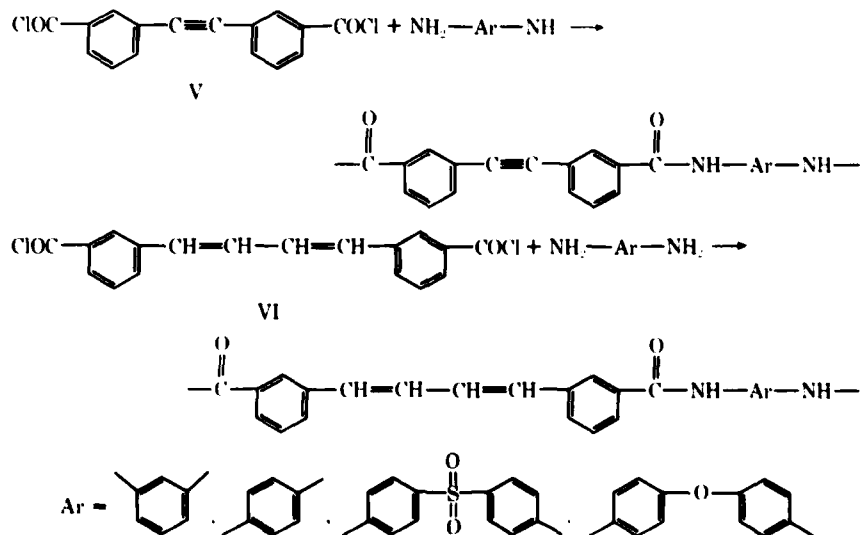
The softening temperature of the polymers before and after curing was measured with a Vicat-type apparatus under a load on the sample of 44 psi at a heating rate of 1°C/min.

Glass Transition Temperature

The second-order transition temperature was measured with a differential scanning calorimeter (Perkin-Elmer DSC-1B) at slope 2 and range 8 with a scan speed of 10°C/min.

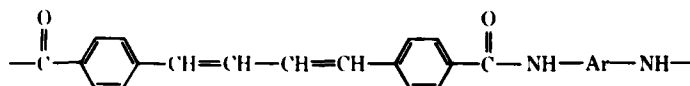
RESULTS AND DISCUSSION

Polyamides were prepared from the acid chloride of bis-*m*-carboxyphenyl acetylene (V) and 1,4-bis-*m*-carboxyphenyl-1,3-butadiene (VI) and aromatic diamines.



The polyamides were purified by dissolution in a minimum amount of dimethylformamide, precipitated with methanol, filtered, washed with methanol, and dried at 100°C in a vacuum oven for 24 hr. Purified polyamides were soluble in dimethylformamide that contained 5% lithium chloride and dimethylacetamide but were only partly soluble in concentrated sulfuric acid. The infrared (IR) spectrum showed absorption at 1660 cm^{-1} for the amide group. Elemental analysis of the polyamides gave correct results for hydrogen, nitrogen, and sulfur, whereas for some unknown reason the analysis for carbon for polymers P-I to P-VIII was lower than the expected theoretical value (see Table I). On combustion these polymers left no residue.

Surprisingly, the viscosities of the polyamides were low. Lowering the temperature or increasing the time of the polymerization did not improve the viscosity. A DSC thermogram showed one peak for the polyamides, which increased very little after curing. All the polyamides exhibited high softening temperatures before curing. After curing no softening temperature below 500°C was measured. The percentage weight loss of the sample before and after curing was quite low, except for polymers P-III and P-IV (see Table II). Polyamides obtained from the acid chloride of 1,4-bis-*p*-carboxyphenyl-1,3-butadiene had previously been completely insoluble in all solvents, whereas the corresponding *m*-isomer described here gave soluble polyamides.



The same solubility behavior was observed in the diene monomers and meta and para isomers.^{2,3} Although there was no trend in properties of the polyamides because of the structural contribution of the aromatic diamines, the polymer obtained from *p*-diaminobenzene proved to be the best in the series. The polyamides that contained oxydiphenyl group (P-IV and P-VIII) showed lower viscosities and thermal properties.

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